IV. *Examination of the proximate Principles of some of the Lichens.*

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Received January 27,—Read February 3, 1848.

THE examination of the proximate principles of the lichens, especially of those which yield red colouring matters with ammonia, attracted the attention of some very eminent chemists at a comparatively early period in the history of organic chemistry, and by the labours of Messrs. ROBIQUET, HEEREN, DUMAS and KANE, very considerable progress was made in their investigation. Within the last four or five years, Messrs. SCHUNCK, ROCHLEDER, HELDT and KNOP have resumed the subject and greatly extended our acquaintance with this interesting but rather difficult department of organic research. It is but justice to Mr. SCHUNCK to state that he has been by far the most successful cultivator of this field, and that he has done more to elucidate it than any of his predecessors.

Nearly two years ago my attention was directed by Dr. PEREIRA to a kind of Orcella weed which had been recently imported into London from the Cape of Good Hope, but which had been rejected by the London archil manufacturers as unfit for their use, from the small quantity of colouring matter it yielded when subjected to the usual process. The lichen was of considerable size, from eight to ten inches long, and was pronounced by an eminent botanist, Dr. SCOULER of Dublin, to whom I submitted it, to be merely a large variety of the *Roccella tinctoria*. I soon ascertained on a very cursory examination, why the lichen had been rejected by the archil makers, for it only contained a small portion of a crystalline principle which yields a red colour with ammonia; I found in its stead, however, a considerable quantity of another crystalline body on which ammonia had no action, and which appeared to have been hitherto undescribed. As it seemed important to ascertain whether or not the red dyes obtained from the various lichens resulted from the action of ammonia on the same crystalline principle, described by Mr. SCHUNCK under the name of Lecanorin, I procured quantities of the several lichens usually employed by the archil makers, and subjected them to investigation. These lichens consisted,—1st, of a large species of *Roccella tinctoria* from the west coast of South America; 2nd, of the *R. tinctoria* from the Cape of Good Hope; 3rd, of the *R. Montagnei* from Angola; and 4th, of the *Lecanora tartarea*. I had made considerable progress with the investigation of these lichens, and also with that of the *Evernia prunastri*, when Mr. SCHUNCK's elaborate paper on the Angola lichen appeared, from which it was evident that at least two varieties of the red colouring principle existed in these lichens. I now therefore proceed to give a detail of the results of these examinations.

I. *The South American variety of* Roccella tinctoria.

This lichen, which is imported in considerable quantities from the west coast of South America, is found, I have reason to believe, in the neighbourhood both of Lima and of Valparaiso. It is a large and handsome lichen from six to eight inches long, and its stems are in some instances as thick as those of a goose-quill. It was pronounced by Dr. Scouler to be a large variety of the *R. tinctoria*. The lichen, after being cut into small pieces, was macerated with a considerable quantity of water for some hours, so as to moisten it completely; a quantity of quicklime was then put into the liquid; the whole was well-stirred and then suffered to repose. The clear liquid, which had a slightly yellow colour, was then drawn off and filtered. The mixture of the lime and lichen had about half as much water poured on it as before, and after standing for a quarter of an hour this was also drawn off, filtered and mixed with the first quantity. In order to exhaust the lichen completely, it should be treated with a considerable excess of lime, but care should be taken not to permit the lichen to remain very long in contact with the lime, otherwise the colouring principle will be oxidized and rendered brown. An excess of muriatic acid was then added to the lime solution, when the whole of the colouring principle of the lichen was precipitated as a white gelatinous bulky mass. When this gelatinous precipitate had been repeatedly washed by decantation to remove adhering muriatic acid, it was collected on a cloth filter, and dried upon a plate of gypsum. When pretty well freed from moisture, it was dissolved in hot spirits of wine, but at a temperature much under boiling, as otherwise an ether compound would have been formed. On the cooling of the solution, the colouring principle was deposited in small white prismatic needles arranged in stars. Should these crystals not be quite colourless, they may be easily rendered perfectly so by redissolving them in alcohol, and digesting them with a little purified animal charcoal. The above is the best process for procuring the colouring principle of this lichen, to which I shall give the name of Orsellic acid, in a state of purity. Orsellic acid may also be obtained, but much less economically, as the greater portion of it is then destroyed, by boiling the lichen in large quantities of water, and then purifying the precipitate obtained by repeatedly crystallizing it out of weak spirit. This is the process by which Mr. Schunck has extracted erythric acid from the Angola lichen. Besides the great loss of the acid which this method occasions, I have always found that the orsellic acid extracted by hot water, even after repeated crystallizations out of alcohol, is never free from traces of a resinous matter and of a fatty acid, which I could only remove by dissolving it in cold lime or baryta water, and purifying it in the way already described.

(*Alpha*) *Orsellic Acid.*

Orsellic acid is nearly insoluble in cold water, but it dissolves, though sparingly, in boiling water, from which it is deposited in small prisms arranged in stars. It is

pretty soluble in cold alcohol and ether, and very readily so in boiling alcohol. Its solutions redden litmus paper very distinctly, and it neutralizes the alkalies and alkaline earths, forming soluble and crystallizable salts. Its most characteristic reaction, by which its presence can be very readily detected, is the deep blood-red colour it instantly strikes when it is brought in contact with a solution of hypochlorite of lime. The red colour only remains for a minute or two, and then changes to a deep yellow, which also gradually disappears. This is a property which orsellic acid possesses in common with most of the red colouring principles of the lichens with which we are acquainted. The orsellic acid is rapidly oxidized by contact with the hypochlorite of lime, and is converted into a dark green uncrystallizable resin. This reaction of hypochlorite of lime on these colouring principles forms a very beautiful class experiment. It may be readily shown by pouring a weak solution of bleaching powder into a basin containing either an alkaline or an alcoholic solution of the lichen, or perhaps best of all, simply on the gelatinous precipitate itself. The only precaution to be observed is that no free acid be present. A solution of orsellic acid in ammonia on exposure to the air soon assumes a bright red colour, which gradually becomes darker and more purple-coloured on standing. When heated on platinum foil, it burns with a yellowish flame, leaving no residue; when it is distilled, it yields a little empyreumatic oil and orcin.

Orsellic acid gives a copious white precipitate with ammonio-nitrate of silver, which however is soon decomposed. It is also precipitated by basic, but not by neutral acetate of lead.

I. 0·216 grm. acid dried at 212° Fahr. and burned with chromate of lead, gave 0·475 carbonic acid and 0·098 water.

II. 0·233 grm. acid gave 0·521 carbonic acid and 0·105 water.

III. 0·3033 grm. acid gave 0·676 carbonic acid and 0·1361 water.

	Calculated numbers.		I.	II.	III.
32 C	2445·920	60·46	60·00	60·98	60·78
16 H	199·672	4·93	5·03	5·00	4·98
14 O	1400·000	34·61	34·97	34·02	34·24
	4045·592	100·00	100·00	100·00	100·00

These analyses give $C_{32}\ H_{15}\ O_{13}+HO$ for the rational formula of hydrated alpha-orsellic acid.

The Baryta Salt.

In order to form the baryta salt, pure orsellic acid was dissolved in a slight excess of cold baryta water, and a current of carbonic acid gas was passed through the solution till all excess of baryta was removed. The precipitate, which consisted of carbonate of baryta and the organic acid, was collected on a filter and dried. It was then treated with hot alcohol, which dissolved out the salt and deposited it on cooling in small shining crystals arranged in stars.

(Alpha) Orsellate of Baryta.

I. 0·593 grm. salt gave 0·149 carb. of barytes=0·1156 BaO=19·49 per cent. BaO.
II. 0·350 grm. salt gave 0·088 carb. of barytes=0·0682 BaO=19·49 per cent. BaO.
III. 0·505 grm. salt gave 0·126 carb. of barytes=0·0977 BaO=19·34 per cent. BaO.

I. 0·1505 grm. salt gave 0·264 carbonic acid and 0·052 water.
II. 0·5773 grm. salt gave 1·041 carbonic acid and 0·197 water.

	Calculated numbers.		Found numbers. I.	II.	III.
32 C	2445·9200	50·01	49·36	49·18	
15 H	187·1925	3·82	3·83	3·79	
1 BaO	956·8800	19·57	19·49	19·49	19·34
13 O	1300·0000	26·60	27·32	27·54	
	4889·9925	100·00	100·00	100·00	

These analyses give $C_{32} H_{15} O_{13}+BaO$ for the formula of orsellate of baryta.

(Alpha) Orsellesic Acid.

When the gelatinous precipitate thrown down from the lime solution of the lichen by muriatic acid, and which constitutes crude orsellic acid, is mixed with a little water, and is again cautiously neutralized by the addition of small quantities of lime or baryta, and boiled till the whole is dissolved, the orsellic acid quickly undergoes a rather singular decomposition. Great care must be taken that no excess of base is present, and the boiling continued till the solution becomes quite clear, which shows that the decomposition of the orsellic acid is complete. If the solution has been quite neutral, no precipitation of carbonate of lime takes place. The liquid is allowed to cool and is then filtered. It is next neutralized with muriatic acid, which throws down an abundant gelatinous precipitate, which is a new acid, to which I shall give the name of orsellesic acid. This precipitate is to be collected on a filter and washed with cold water to remove adhering muriatic acid. It is then to be dried and dissolved in weak spirits, out of which it readily crystallizes. It is to be still further purified by being digested with animal charcoal in water, which, for a reason to be presently mentioned, must not be allowed to boil. The acid crystallizes out of alcohol and water in perfectly white needle-shaped crystals arranged in stars. It reddens litmus paper distinctly, and has a feebly acid and somewhat bitter taste. It is very soluble in alcohol, both hot and cold; is much more soluble in hot water than orsellic acid, and crystallizes out of its aqueous solutions in much larger crystals. When orsellesic acid is boiled in water it gives off carbonic acid, and is pretty rapidly converted into orcin, which, when the solution is concentrated, is deposited in perfectly colourless crystals. About half an hour's boiling is sufficient to convert any quantity of orsellesic acid into perfectly colourless orcin. When orsellesic acid, on the other hand, is boiled with an excess of lime or baryta, it is also converted into

orcin with the deposition of a carbonate of the base, and the formation of a reddish colouring matter, from which the orcin can never be effectually freed. This subject will be again referred to in a subsequent part of the paper. Orsellesic acid gives a fugitive bluish red, or rather violet colour with hypochlorite of lime, thus differing from the reaction of orsellic acid, but not easily distinguishable from that of orcin with the same reagent.

When orsellesic acid is dissolved in ammonia and exposed to the air, it yields a red colouring matter similar to orcein. The acid was dried at 212° FAHR.

I. 0·3313 grm. acid gave with chromate of lead 0·7045 carbonic acid and 0·1567 water.

II. 0·3301 grm. acid gave 0·7008 carbonic acid and 0·151 water.

	Calculated numbers.		I.	II.
16 C	1222·960	57·27	57·99	57·90
9 H	112·315	5·26	5·25	5·08
8 O	800·000	37·47	36·76	37·02
	2135·275	100·00	100·00	100·00

These analyses give $C_{16} H_8 O_7 + HO$ as the rational formula of hydrated orsellesic acid.

(*Alpha*) *Orsellesiate of Baryta.*

The baryta salt was prepared from crude orsellesic acid which had been carefully freed from adhering muriatic acid. The crude orsellesic acid was dissolved in hot spirits, to which small quantities of dry crystals of baryta were cautiously added. The solution of the salt may be concentrated by evaporation so long as it is acid, but any excess of base must be avoided, as otherwise the acid would be decomposed and carbonate of baryta deposited. When the hot solution has been sufficiently concentrated, it should be carefully neutralized while hot, and set aside to crystallize. The salt is exceedingly soluble both in water and in spirits. When evaporated to the consistence of a syrup, it crystallizes in small prisms; but when the spirits have been much diluted, the salt is deposited in long four-sided prisms. Its aqueous solutions must be evaporated *in vacuo*. As the baryta salt is decomposed when kept at 212° F., it was also dried *in vacuo*. Six or seven days were required for this purpose, and it lost from seven to eleven per cent. of water, according to the strength of the spirits out of which it had crystallized.

Per cent.

I. 0·342 grm. salt gave 0·1407 carb. of baryta = 0·1091 BaO = 31·90 BaO.

II. 0·221 grm. salt gave 0·091 carb. of baryta = 0·0706 BaO = 31·94 BaO.

III. 0·293 grm. salt gave 0·120 carb. of baryta = 0·0931 BaO = 31·77 BaO.

0·4915 grm. salt gave 0·7442 carbonic acid and 0·161 water.

	Calculated numbers.		I.	II.	III.
16 C	1222·960	41·04	41·29		
8 H	99·836	3·35	3·63		
1 BaO	956·880	32·11	31·90	31·94	31·77
7 O	700·000	23·50	23·18		
	2979·676	100·00	100·00		

These numbers give $C_{16} H_8 O_7 + BaO$ for the rational formula of orsellesiate of baryta.

Orsellesic Ether.

When (alpha) orsellic acid is boiled for some hours in strong alcohol an ether compound is formed. This ether is most advantageously prepared from the gelatinous precipitate obtained from the lime solution by muriatic acid. This precipitate, when it has been cautiously dried, is to be boiled for six or seven hours in strong alcohol. The solution is then to be cautiously evaporated on the water-bath till nearly the whole of the alcohol has been driven off; care, however, being taken not to evaporate it to dryness, otherwise much of the ether would be converted into a resinous matter. The residue is then to be boiled with a considerable quantity of water and filtered. On the cooling of the liquid the ether precipitates in long flat needles, which have at first a yellowish colour from adhering resin, but when they are treated with animal charcoal and recrystallized they are quite colourless. This ether cannot be distinguished in its external properties from the lecanoric and the erythric ethers. When it is distilled with dry potash it gives off alcoholic vapours, and orcin remains in the retort. Its reactions with ammonia and hypochloride of lime are similar to those of orsellesic acid. It might naturally have been expected that, as orsellic acid was the acid employed in its formation, this ether would have been the orsellic ether. From the results of the subjoined analysis I have been unable to deduce the formula which the orsellic ether ought theoretically to have, while the analyses agree pretty well with the formula of the orsellesic ether.

I am therefore disposed to regard this compound as the orsellesic ether, the more so as I have ascertained that by merely boiling orsellic acid in water without the presence of a base, it is resolved into orsellesic acid. In a subsequent part of this paper, in the case of evernic acid, an instance of the formation of an ether of a second acid different from that of the acid originally put into the alcohol appears to occur.

I. 0·327 grm. ether dried at 212° Fahr., gave 0·734 carbonic acid and 0·1842 water.

II. 0·3195 grm. ether gave 0·716 carbonic acid and 0·177 water.

	Calculated numbers.		Found numbers. I.	Found numbers. II.
20 C	1528·700	61·38	61·24	61·13
13 H	162·233	6·51	6·26	6·15
8 O	800·000	32·11	32·50	32·72
	2490·933	100·00	100·00	100·00

The rational formula of orsellesic ether, therefore, appears to be $C_{16} H_8 O_7 + C_4 H_5 O$.

Roccella tinctoria *from the Cape of Good Hope.*

This lichen, the history and botanical characters of which were partially described in a previous part of this paper, was pronounced by Dr. SCOULER to be also a large variety of the *Roccella tinctoria.* It contains two crystalline principles, one very similar to orsellic acid, and another with much less determinately acid characters, to which I have given the provisional name of roccellinin. These two principles may be both extracted by treating the lichen with milk of lime, and precipitating with muriatic acid in the way already described. The gelatinous mass which precipitates consists of a mixture of both principles; but they may be easily separated, as the roccellinin is quite insoluble both in cold and in hot water, while the acid analogous to orsellic acid, and which I purpose to call (beta) orsellic acid, is pretty readily soluble in boiling water. By repeatedly treating therefore the mixture of the two substances with boiling water and filtering, the (beta) orsellic acid is dissolved and deposited on the cooling of the liquid in small silky crystals. These crystals may be obtained quite white and of a much larger size by repeatedly crystallizing them out of weak spirits, care being taken not to boil the solutions. The (beta) orsellic acid may also be prepared by boiling the lichen repeatedly with water, in the way already described for (alpha) orsellic acid. The orsellic acid prepared by this process crystallizes in small silky needles, which are quite free from roccellinin, but which still retain traces of a fatty acid and a little resin, from which I could only purify them by dissolving them in lime or baryta water, precipitating by muriatic acid, and treating them in the way already described.

(*Beta*) *Orsellic Acid.*

The following are the characters of (beta) orsellic acid when purified by repeated crystallizations out of weak spirits. Its aqueous and alcoholic solutions redden litmus paper. It is soluble in hot and cold alcohol, and in ether. A solution of hypochlorite of lime yields the same fugitive blood-red colour with it as with (alpha) orsellic acid, with erythric acid, and with the colouring principle in *Lecanora tartarea.* The action of ammonia on all these bodies appears perfectly similar. (Beta) orsellic acid yields but a trifling precipitate with acetate, but a bulky white precipitate with subacetate of lead. In short, it is intermediate in its properties between (alpha) orsellic acid and erythric acid, but approaches the former more closely.

I. 0·2535 grm. acid dried at 212° FAHR., gave with chromate of lead 0·558 carbonic acid and 0·1155 water.

II. 0·2555 grm. substance gave 0·564 carbonic acid and 0·121 water.

	Calculated numbers.		Found numbers.	
			I.	II.
34 C	2598·790	60·10	60·07	60·20
18 H	224·631	5·19	5·06	5·26
15 O	1500·000	34·71	34·87	34·54
	4323·421	100·00	100·00	100·00

The rational formula of the hydrated (beta) orsellic acid is $C_{34}, H_{17}, O_{14}+HO$.

Baryta Salt.

The baryta salt of (beta) orsellic acid is prepared in exactly the same way as the (alpha) orsellate of baryta, by dissolving the acid in an excess of baryta water in the cold, removing the excess of baryta by a stream of carbonic acid gas, collecting the precipitates on a filter and drying them.

The organic salt was then separated from the carbonate of baryta by means of hot alcohol, out of which it crystallized in small white prismatic needles.

Per cent.

I. 0·237 grm. salt gave 0·067 $BaOSo_3$=0·0439 BaO=18·52 BaO.

II. 0·357 grm. salt gave 0·101 $BaOSo_3$=0·0662 BaO=18·54 BaO.

0·346 grm. salt gave with chromate of lead 0·6275 carbonic acid and 0·1285 HO.

	Calculated numbers.		Found. I.	II.
34 C	2598·7900	50·29	49·46	
17 H	212·1515	4·15	4·12	
1 BaO	956·8800	18·51	18·52	18·54
14 O	1400·0000	27·05	27·90	
	5167·8215	100·00	100·00	

The rational formula of the salt is $C_{34}\,H_{17}\,O_{14}+BaO$.

When (beta) orsellic acid is exactly neutralized with lime or baryta and boiled for a short time, it is decomposed just as (alpha) orsellic acid is when similarly treated, yielding a crystallizable acid, which I shall call (beta) orsellesic acid, whose properties very closely resemble those of (alpha) orsellesic acid. (Beta) orsellesic acid also forms a very soluble baryta salt, which crystallizes in long four-sided prisms. When an aqueous solution of (beta) orsellesic acid is boiled, it gives off carbonic acid and is wholly resolved into colourless orcin, exactly in the same way as (alpha) orsellesic acid. A more precise examination of this and another corresponding acid derived from erythric acid will form the subject of a future communication.

An ether compound may be readily procured by boiling pure (beta) orsellic acid in strong alcohol, evaporating the solution, and treating the residue with boiling water in the way already described for orsellesic ether. It may also be prepared by boiling the crude precipitate already mentioned, consisting of orsellic acid and roccellinin, when dried, in strong spirits. In this case the ether is apt to contain a little roccellinin, but from this it can be easily separated by crystallizing it out of boiling water, in which the roccellinin is nearly insoluble. The ether compound crystallizes on the cooling of the liquid in long flat prisms, which cannot be distinguished in appearance from the orsellesic, lecanoric or erythric ethers, with which bodies in its properties and reactions it very closely corresponds.

I. 0·365 grm. ether dried at 212° Fahr., gave with chromate of lead 0·814 carbonic acid and 0·206 water.

II. 0·396 grm. ether gave 0·882 carbonic acid and 0·219 water.

III. 0·2515 grm. ether gave 0·561 carbonic acid and 0·142 water.

	I.	II.	III.
C	60·82	60·75	60·83
H	6·27	6·15	6·27
O	32·91	33·10	33·00
	100·00	100·00	100·00

This substance when distilled with caustic potash gave off alcoholic vapours, leaving orcin in the retort. It is certainly an ether, but of what acid I am unable to determine. These analyses do not agree with the formula of (beta) orsellic ether. It is not improbable therefore that it is the ether of (beta) orsellesic acid, but this is a point which can only be determined when that acid has been subjected to analysis.

Roccellinin.

The Cape of Good Hope lichen contains a much larger quantity of roccellinin than of (beta) orsellic acid. The most convenient mode of extracting the roccellinin is by drying the gelatinous mass precipitated from the lime solution of the lichen by muriatic acid, and then boiling it for a considerable time in strong spirits. The orsellic acid is generally converted into the ether compound, while the roccellinin remains unchanged. On evaporating the solution nearly to dryness, and then treating the residue with boiling water, the ether compound is readily removed, while the roccellinin remains undissolved. By boiling the roccellinin in a large quantity of strong spirits it also dissolves, and on the cooling of the liquid it is deposited in long white hair-like crystals. By repeated crystallizations out of strong spirits, aided by a little animal charcoal, the roccellinin is rendered perfectly pure. It consists of soft hair-like crystals of a silky lustre, and about half an inch long, usually arranged in stars. If these crystals, when treated with hypochlorite of lime, acquire a reddish tinge, they are impure, from containing a little adhering orsellic acid. When quite pure, hypochlorite of lime gives them a greenish-yellow colour, which is permanent. Roccellinin requires a considerable quantity of boiling alcohol to dissolve it, and it is but very moderately soluble either in cold alcohol or in ether. It dissolves readily in the fixed alkalies and in ammonia. Its solutions remain quite colourless. When roccellinin is boiled in baryta water no carbonate of baryta is deposited, and a hot solution of caustic potash is equally inoperative upon it. When it is boiled in alcohol, saturated with muriatic acid gas, no ether is produced.

I. 0·406 grm. substance dried at 212° Fahr., gave with chromate of lead 0·9328 CO_2 and 0·1785 water.

II. 0·351 grm. gave 0·807 carbonic acid and 0·156 water.

III. 0·4705 grm. gave 1·079 carbonic acid and 0·205 water.

IV. 0·4695 grm. gave 1·075 carbonic acid and 0·1965 water.

		Calculated numbers.	I.	II.	III.	IV.
38 C	2904·5300	62·91	62·66	62·67	62·54	62·44
17 H	212·1515	4·59	4·88	4·90	4·84	4·65
15 O	1500·0000	32·50	32·46	32·43	32·62	33·01
	4616·6815	100·00	100·00	100·00	100·00	100·00

The results of these analyses agree pretty closely with the formula $C_{38}H_{17}O_{15}$, which however is merely empirical. I have made many attempts to determine the atomic weight of roccellinin by endeavouring to combine it with the alkalies and earths so as to form definite salts, but hitherto without success. It produces no precipitate with acetate or subacetate of lead, or with nitrate or ammonio-nitrate of silver. When a current of chlorine gas was passed for four days through a quantity of roccellinin diffused through water, the roccellinin assumed a slightly yellow colour. It was collected on a filter and washed to free it from adhering muriatic acid; when crystallized out of alcohol its properties were unchanged, and when subjected to analysis it contained no chlorine. Nitric acid in the cold had no action upon it, with the assistance of heat it converted it into oxalic acid. An attempt was made to prepare a baryta salt by boiling the roccellinin with freshly-precipitated carbonate of baryta. A quantity of prismatic crystals were obtained, but the quantity of base they contained varied according to the concentration of the solution. With caustic baryta, magnesia and lime, the results were equally unsatisfactory. When dissolved in an excess of ammonia and dried *in vacuo*, it was found to be unchanged, and to contain no ammonia. Roccellinin appears therefore to be a very indifferent body, which, like santonin, enters into no stable combinations with either alkalies or acids, though it appears to have a slight affinity for bases, and may therefore be regarded as a feeble acid. I am quite unable to determine what relation roccellinin bears to the orsellic series of acids, with which, however, it is not improbably connected, as the (beta) orsellic acid appears to be partially replaced by it in the Cape of Good Hope lichen.

Roccella Montagnei.

This lichen, which is imported in large quantity from the Portuguese settlement of Angola, and also from Madagascar, where it grows upon trees, was examined by Mr. Schunck under the name of *Roccella tinctoria* var. *fuciformis*. Dr. Scouler pronounces it to be the *R. Montagnei* of Betenger, who* found it growing on mango trees at Madras. The branches of the true *R. fuciformis* are much rounder than those of the *R. Montagnei*, which are nearly quite flat. This lichen is by much the richest in colouring matter of any of those employed by the archil manufacturers. Mr. Schunck extracted its colouring principle by treating the lichen with boiling water, and purifying the crystalline precipitate by repeatedly crystallizing it out of weak spirits. This is a very wasteful process; Mr. Schunck states that he only got 60 grs. of erythric acid from a pound weight of lichen. The erythric acid employed in my experiments was prepared partly in this way, but chiefly by the more economical method of macerating the lichen in milk of lime, as already described. By the lime process, the average product of crude erythric acid amounted to twelve per cent. of the weight of the lichen employed. The erythric acid prepared by either method

* See Voyage aux Ind. Orient.

had similar properties, and when subjected to analysis gave identical results. I regret to add that in all my analyses, amounting to about a dozen, I always obtained about one and a half per cent. less carbon than Mr. SCHUNCK, though the combustions were made with all possible care, and a stream of oxygen gas was sent through the apparatus towards the close of the operation. The alcoholic and aqueous solutions of erythric acid do not redden litmus paper, its acid properties are therefore rather feeble. Erythric acid agrees with (alpha) and (beta) orsellic acids in yielding red-coloured compounds with ammonia, and also in its reaction with hypochlorite of lime. There is, generally speaking, a great similarity among these bodies in their behaviour towards reagents; still their atomic weights and the products of their decompositions are very different.

I. 0·5951 grm. acid dried at 212° FAHR., gave with chromate of lead 1·2404 Co_2 and 0·298 HO.

II. 0·3846 grm. gave 0 8031 carbonic acid and 0·1846 water.

III. 0·6737 grm. gave 1·4115 carbonic acid and 0·3415 water.

	Calculated numbers.		I.	II.	III.
C 20	1528·7000	57·34	56·85	56·94	57·14
H 11	137·2745	5·15	5·56	5·33	5·63
O 10	1000·0000	37·51	37·59	37·73	37·23
	2665·9745	100·00	100·00	100·00	100·00

These analyses give $C_{20}\,H_{10}\,O_9 + HO$ for the formula of hydrated erythric acid.

I made repeated attempts to form the lead salt, but I could not obtain it of a constant composition. I had no better success with an attempt to form a baryta salt. When erythric acid was dissolved in an excess of baryta in the cold, and a stream of carbonic acid gas sent through the solution, the whole of the baryta was thrown down in the state of carbonate. This plainly shows that erythric acid is a much feebler acid than either of the orsellic acids.

Erythric Ether.

Erythric ether may be readily obtained by boiling the crude acid in strong spirits. It is crystallized out of water and purified in the same way as orsellesic and lecanoric ethers, which substances it very closely resembles in appearance and properties.

I. 0·4646 grm. ether dried at 212° FAHR., gave 1·032 carbonic acid and 0·265 water.

II. 0·372 grm. substance gave 0·8285 Co_2 and 0·2115 water.

	Calculated numbers.		I.	II.
24 C	1834·440	60·70	60·65	60·74
15 H	187·192	6·19	6·33	6·31
10 O	1000·000	33·11	33·02	33·05
	3021·632	100·00	100·00	100·00

The rational formula for erythric ether therefore is $C_{20}\,H_{10}\,O_9 + C_4\,H_5\,O$.

Erythric ether combines with basic acetate of lead. This compound is readily obtained by adding a hot solution of basic acetate of lead to a solution of the ether in boiling water. It falls as a bulky white precipitate. It was washed and dried at 212° Fahr.

Per cent.

I. 1·5145 grm. salt gave 0·5545 PbO and 0·4805 metallic lead=70·78 oxide.

II. 1·0825 grm. salt gave 0·3000 PbO and 0·4295 Pb =71·01 oxide.

I. 0·7188 grm. salt gave with chromate of lead 0·491 Co_2 and 0·1075 water.

II. 1·504 grm. salt gave with chromate of lead 1·043 carbonic acid and 0·232 water.

	I.	II.
C	18·63	18·91
H	1·66	1·71
PbO	71·01	71·01
O	8·70	8·37
	100·00	100·00

I have been quite unable to deduce any rational formula from these analyses of the lead compound of this ether, though the combination appears to be a very stable one, as the salt prepared at different times had always the same composition.

Erythric Methylic Ether.

The methyle compound is readily obtained by boiling erythric acid in strong wood spirit. It crystallizes in longer and narrower prisms than erythric ether. The reactions of both bodies with ammonia and hypochlorite of lime are perfectly similar.

I. 0·4205 grm. ether gave 0·9144 carbonic acid, and 0·209 water.

II. 0·3285 grm. gave 0·715 carbonic acid and 0·1685 water.

	Calculated numbers.		I.	II.
22 C	1681·570	59·14	59·30	59·36
13 H	162·233	5·70	5·52	5·69
10 O	1000·000	35·16	35·18	35·04
	2843·803	100·00	100·00	100·00

The rational formula of erythrate of methyle is $C_{20}H_{10}O_9+C_2H_3O$.

When the ethyl compound of erythric acid is boiled with caustic potash or baryta, alcoholic vapours are given off, and orcin and another crystalline body, pseudo-orcin, remain in the solution.

When erythric acid is exactly neutralized with lime or baryta and boiled for a short time it is decomposed, two new compounds being formed, one an acid, which is very similar in appearance and properties to (alpha) and (beta) orsellesic acids, and the other is picro-erythrin. The quantity of the new acid, which I shall call erythrelesic acid, which erythric acid yields, is much less than what is obtained when either of the orsellic acids is decomposed in a similar manner. The reason of this appears to be that a large portion of the erythric acid goes to the formation of the

picro-erythrin, while in the case of the orsellic acids, orsellesic acid and some carbonic acid are the only products. Erythrelesic acid is not quite so soluble in water as either of the orsellesic acids; it crystallizes in small flat scales. When erythrelesic acid is boiled for a short time in water, it is, like the two preceding acids, converted wholly into colourless orcin with evolution of carbonic acid gas. When, on the other hand, it is boiled with an excess of lime or baryta, it is also converted into orcin, which, by this process, has always a deep red colour. Erythrelesic acid forms a very soluble salt with baryta, which crystallizes in long four-sided prisms, which are flatter than those of orsellate of baryta. I intend subjecting this and its kindred acids to a more minute examination. The taste of erythrelesic acid is sourer and more bitter than the orsellesic acid, and it exhibits the same violet colour with hypochlorite of lime.

Picro-erythrin.

When erythric acid has been neutralized by lime or baryta and boiled, as above described, and the erythrelesic acid thrown down by muriatic acid, and removed, the mother-liquor contains a considerable amount of picro-erythrin. When the mother-liquor is concentrated considerably and set aside for a few days in a cold place, the picro-erythrin is deposited in yellowish-coloured crystals. These may be purified by washing them with cold water, and repeatedly crystallizing them out of boiling water, aided by a little animal charcoal. When pure, picro-erythrin crystallizes in long colourless needles arranged in stars. It has a very bitter taste, and is exceedingly soluble in hot water, but very slightly soluble in cold water. Picro-erythrin strikes the same blood-red colour with hypochlorite of lime as erythric acid does. Its solutions in ammonia, on standing for some time exposed to the air, yield a red compound similar to orcein.

I. 0·5225 grm. picro-erythrin dried at 212° Fahr. and burned with chromate of lead, gave 1·0169 carbonic acid and 0·286 water.

II. 0·2825 grm. picro-erythrin gave 0·5527 Co_2 and 0·1513 water.

		Calculated numbers.	Found. I.	Found. II.
34 C	2598·790	53·19	53·07	53·23
23 H	287·028	5·87	6·08	5·95
20 O	2000·000	40·94	40·85	40·82
		100·00	100·00	100·00

The formula which I have found for picro-erythrin differs from Mr. Schunck's by one atom of hydrogen, his being $C_{34} H_{24} O_{20}$.

I was unable to procure the lead salt, mentioned by Mr. Schunck, of uniform composition, though I made repeated attempts. I was not more successful in my endeavours to form a baryta salt; the picro-erythrin crystallized out of its solution, retaining scarce a trace of baryta. Mr. Schunck's description of the other properties

of picro-erythrin are generally speaking very correct, but he has fallen into one or two errors. Mr. SCHUNCK supposes that picro-erythrin is formed from erythric acid by that acid merely taking up five equivalents of water. Now, I have fully ascertained that erythric acid is never converted into picro-erythrin without the evolution of a considerable amount of carbonic acid gas, so that in this process carbon is always eliminated, and the change is not produced merely by the absorption of the elements of water. Picro-erythrin is a very stable body; a quantity of it after being boiled in water for thirty-six hours had undergone very little change, a very small portion of it only having been converted into orcin, and probably into pseudo-orcin. Mr. SCHUNCK asserts that when picro-erythrin is boiled with an excess of lime or baryta it is wholly converted into orcin. A small quantity of orcin is always produced by this process, but the great bulk of the compound then formed is a new sweet crystallizable body to be described in the next section, and which I shall call pseudo-orcin.

Pseudo-orcin.

I have as yet only succeeded in obtaining this very curious substance from erythric acid and its compounds, by acting on them with alkalies. As already mentioned, it is only from picro-erythrin itself, or from the portion of erythric acid which yields picro-erythrin, that pseudo-orcin is obtained. Erythrelesic acid does not yield a trace of it. The best way of preparing pseudo-orcin in quantity is the following. The lime solution of the *Roccella Montagnei* should be boiled in an open pan for two or more hours, and the liquid concentrated to a third or a fourth of its bulk. A stream of carbonic acid gas should be sent through the liquid so long as carbonate of lime is precipitated, and the liquid filtered and evaporated on the water-bath to a thick syrup. This syrup consists chiefly of orcin and pseudo-orcin, with much reddish colouring matter containing a good deal of resin. The syrup should then be introduced into a flask, and treated with a large quantity of ether, which dissolves the orcin and most of the colouring matter, leaving the pseudo-orcin undissolved. A more economical proceeding is to mix the syrup with three times its bulk of alcohol. After standing for a couple of days the pseudo-orcin crystallizes out in small shining crystals. These crystals should be collected on a cloth filter, pressed, and washed with cold strong spirits, which removes most of the colouring matter and any adhering orcin. On being crystallized twice or thrice out of strong boiling spirits, the pseudo-orcin is obtained in large shining colourless crystals. Pseudo-orcin may be obtained in still finer crystals by crystallizing it out of water, in which liquid it is exceedingly soluble, much more so than in spirits. I have obtained it from its aqueous solutions in curiously truncated pyramids, nearly an inch broad, having a brilliant diamond lustre. In fact, there are very few organic substances which form more splendid crystals than pseudo-orcin. I sent a quantity of these crystals to Professor MILLER of Cambridge, who was so kind as to determine their measurements and optical properties. The following are the results of his examination:—

Pyramidal . . . . 111, $\bar{1}\,\bar{1}1 = 38° 58'$
Simple forms . . . . . a 100, r 111 s 311.

Fig. 1.

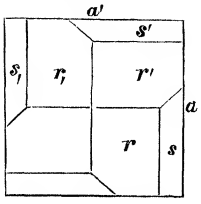
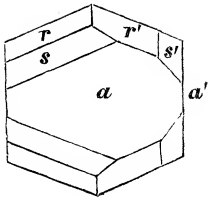


Fig. 2.



The form to which the faces s belong is usually hemihedral with parallel faces, 11 $3\bar{1}\bar{3}$. In two crystals only, out of ten which were examined, faint indications of the faces of the other half form were observed.

The angles between normals to the faces are,—

aa'	90°	0′
ra	70	31
sa	43	18
rr'	38	58
rr_1	56	17
ss_1	100	12

No cleavage observable.

The index of refraction, for the brightest part of the spectrum, of the ordinary ray $=1{\cdot}545$; of a ray in a plane perpendicular to the faces a, a', polarized in that plane $=1{\cdot}523$.

Pseudo-orcin is quite neutral to test paper. It has a very sweet taste, though scarcely so sweet as that of orcin. When heated on platinum foil it burns with a blue flame, and emits a smell similar to caramel. When distilled it yields a thin yellowish liquid, emitting at the same time the smell of burnt sugar. The liquid is soluble both in water and in alcohol; it does not crystallize on standing.

Ammonia and hypochlorite of lime have no action upon pseudo-orcin; neither is it affected by any of the alkalies. It is not acted on by bromine. It is not affected by cold nitric acid, but hot nitric acid converts it into oxalic acid. It is not blackened by cold sulphuric acid, but when heated with that acid it becomes brown. Pseudo-orcin gives no precipitate with neutral or basic acetate of lead, with nitrate or ammonio-nitrate of silver, or with salts of copper. It is incapable of fermentation. Dried *in vacuo*, and then at 212° Fahr., it lost no water.

I. 0·507 grm. dried at 212° Fahr., gave with chromate of lead 0·734 Co_2 and 0·3813 water.

II. 0·6275 grm. dried at 212° Fahr., gave 0·907 Co_2 and 0·467 water.

III. 0·4702 grm. dried at 212° Fahr., gave 0·679 Co_2 and 0·355 water.

	Calculated numbers.		I.	II.	III.
10 C	764·3500	39·67	39·46	39·42	39·36
13 H	162·2335	8·42	8·55	8·30	8·60
10 O	1000·0000	51·91	51·99	52·28	52·04
	1926·5835	100·00	100·00	100·00	100·00

These numbers agree pretty well with the formula $C_{10} H_{13} O_{10}$, which however is merely empirical, as I have been quite unable to form any compound with pseudo-orcin so as to determine its atomic weight. Pseudo-orcin appears to be an exceedingly indifferent substance with properties intermediate between those of orcin and mannite.

Mode of extracting the Colouring Principles of the Lichens employed by the Archil makers, so as to render them more portable for commercial purposes.

The amount of colouring principle contained in even the richest of the lichens employed by the archil manufacturers, bears but a small proportion to the weight of the lichen itself. In the case of the *Roccella Montagnei* from Angola, it amounts to about twelve per cent.; in the South American lichen to about seven; and in the Cape variety and in the *Lecanora tartarea* it varies from about two to one and a half per cent. From the great distances from which most of these lichens must be brought, the cost of their transport is so considerable as materially to diminish their commercial value. This is especially the case with their poorer varieties. I think it would in many cases therefore be found advantageous to extract the colouring matter in the countries where the lichens grow, and as this can be effected very readily, a large proportion of the expense of their transport might be easily saved. All that would be necessary for this purpose would be to cut the lichens into small pieces; to macerate them in wooden vats with milk of lime, and to saturate the solution either with muriatic or acetic acid. The gelatinous precipitate could then be collected on cloths and dried by a gentle heat. Almost the whole of the colouring matter in a lichen could thus be easily extracted at a comparatively small expense, and the value of the dried extract, amounting to more than a thousand pounds per ton, would abundantly defray the expense from even the most distant inland localities, such as the Andes or the Himalayas.

Mode of estimating the quantity of Colouring Matter in the Lichens.

A solution of hypochlorite of lime affords a very ready method of approximating pretty closely to the amount of red colouring matter contained in a lichen. Any convenient quantity of the lichen, say one hundred grains, may be cut into very small pieces and then macerated with milk of lime till all the colouring principle is extracted. Three or four macerations are quite sufficient for this purpose if the lichen has been sufficiently comminuted. The clear liquors should be filtered and mixed together. A solution of bleaching powder of known strength should then be poured into the lime solution from a graduated alkalimeter. The moment the bleaching liquor comes in contact with the lime solution of the lichen, a blood-red colour is produced which disappears in a minute or two, and the liquid has only a deep yellow colour. A new quantity of the bleaching liquid should then be poured into the lime solution and the mixture carefully stirred. This operation should be

repeated so long as the addition of the hypochloride of lime causes the production of the red colour; for this shows that the lime solution still contains unoxidized colouring principle. Towards the end of the process, the bleaching solution should be added by only a few drops at a time, the mixture being carefully stirred between each addition. We have only to note how many measures of the bleaching liquor have been required to destroy the colouring matter in the solution, to determine the amount of the colouring principle it contained. The following are the results of trials with the same test liquor upon four varieties of lichen.

	Measures.
Angola lichen required	200=1·00
American lichen	120=0·60
Cape lichen	035=0·17
Lecanora tartarea from Germany, near Giessen . .	025=0·12

The amount of colouring principle in a lichen may also be directly determined by extracting the lichen with milk of lime, by precipitating by means of acetic acid, collecting the precipitate on a weighed filter, drying it at the ordinary temperature, and then weighing it.

Evernia Prunastri.

This lichen was examined in 1843 by Messrs. Rochleder and Heldt, who found in it a substance which they regarded as identical with lecanoric acid. The results of my examination are so different that I am under the necessity of supposing, either that the proximate principles of the *Evernia Prunastri* which grows in Germany are quite different from those of the same plant in Scotland, or, what is much more probable, that these gentlemen had not examined the true *Evernia Prunastri*, but some other lichen in its stead. The lichen on which I operated was pronounced to be the true *Evernia Prunastri* by Dr. Scouler and by two other botanists to whom I submitted it. The lichen was extracted by milk of lime in the way already so often described. Its solution had a bright yellow colour, and on being neutralized by muriatic acid, it yielded an abundant pale yellow precipitate. This was washed, collected on a filter and cautiously dried. It was then digested, at a temperature much under that of boiling, in a quantity of very weak spirits, and this digestion was repeated several times till about two-thirds of the precipitate had dissolved. On the cooling of the solution a mass of small yellowish crystals was deposited. These crystals were rendered perfectly colourless by being treated with animal charcoal, and by being repeatedly crystallized out of weak spirits. They constitute a new acid, which I purpose to call Evernesic acid. The portion of the precipitate which did not dissolve in the weak spirits is usnic acid, which requires pretty strong boiling alcohol for its solution. The usnic acid will be again referred to at a subsequent part of this paper.

Evernic Acid.

Evernic acid is insoluble in cold water; boiling water dissolves a little of it, which, on the cooling of the liquid, is deposited in white flocks. It is pretty soluble in cold, and exceedingly soluble in hot alcohol; on cooling the liquid is filled with a mass of small adhering needles. Evernic acid is also pretty soluble in ether. This acid has neither taste nor smell. Its alcoholic solution reddens litmus paper. When heated on platinum foil, evernic acid burns readily without leaving any residue; and when it is heated in a test tube, it yields a little empyreumatic oil and a sublimate which has all the characters of orcin. When evernic acid is dissolved in an excess of ammonia and exposed to the air, on standing a few days the liquid slowly assumes a dark red colour. Evernic acid yields only a slightly yellowish colour with hypochlorite of lime. Evernic acid loses no water at 212° Fahr.

I. 0·304 grm. dried at 212° gave with chromate of lead 0·687 Co_2 and 0·137 water.

II. 0·3325 grm. gave 0·7285 carbonic acid and 0·1525 water.

	Calculated numbers.		I.	II.
34 C	2598·790	61·89	61·63	61·61
16 H	199·672	4·75	5·00	5·16
14 O	1400·000	33·36	33·37	33·23
	4198·462	100·00	100·00	100·00

These analyses give $C_{34}\,H_{15}\,O_{13}+HO$ for the rational formula of hydrated evernic acid.

Potash Salt.

A quantity of evernic acid was dissolved in a considerable excess of potash in the cold; the solution had a yellowish colour and frothed like soap. A current of carbonic acid was then sent through the solution till all the caustic potash present was neutralized, when the liquid became filled with a mass of small crystals. These are the potash salt, which is very soluble in caustic potash, but very slightly soluble either in carbonate of potash or in cold water. The crystals were collected on a filter, dried, purified by digestion with animal charcoal, and finally crystallized out of spirits *in vacuo*. The crystals were then perfectly colourless and had a fine silky lustre.

I. 0·0803 grm. salt gave 0·0183 sulphate of potash = 0·098 potash = 12·31 Ko per cent.

II. 0·235 grm. salt gave 0·054 sulphate of potash = 0·0291 Ko = 12·30 Ko per cent.

I. 0·192 grm. salt burned with chromate of lead, gave 0·393 carbonic acid and 0·076 water.

II. 0·319 grm. salt gave 0·6467 carbonic acid and 0·1235 water.

	Calculated numbers.		I.	II.
34 C	2598·7900	55·57	55·82	55·28
15 H	187·1925	4·00	4·39	4·30
13 O	1300·0000	27·82	27·49	28·12
KO	589·9200	12·61	12·30	12·30
	4675·9025	100·00	100·00	100·00

These numbers give $C_{34}\ H_{15}\ O_{13}+KO$ as the formula of evernate of potash. This salt loses no water at 212° F., and appears to be anhydrous.

The Baryta Salt.

The baryta salt was prepared in a way similar to the potash salt, by dissolving the acid in an excess of cold baryta water, and neutralizing the solution by a stream of carbonic acid gas. This salt is but little soluble in water, but very soluble in weak spirits. It crystallizes in small prisms. It was first dried *in vacuo*, and then at 212° F., when it lost no water.

I. 0·207 grm. salt gave 0·049 carb. of baryta =0·038 BaO =18·35 per cent. BaO.

II. 0·1683 grm. salt gave 0·0470 sulphate of BaO =0·0308 BaO =18·30 per cent. BaO.

I. 0·2435 grm. salt gave 0·449 carbonic acid and 0·09 water.

II. 0·2534 grm. salt gave with chromate of lead 0·4675 Co_2 and 0·0·94 water.

	Calculated numbers.		I.	II.
34 C	2598·790	50·40	50·30	50·31
16 H	199·672	3·87	4·10	3·96
14 O	1400·000	27·17	27·08	27·38
BaO	956·880	18·56	18·52	18·35
	5155·342	100·00	100·00	100·00

The rational formula of evernate of baryta appears therefore to be $C_{34}\ H_{15}\ O_{13}$ +BaO+Aq. It contains one atom of water.

Evernesic Acid.

A quantity of evernic acid was dissolved in a slight excess of caustic potash, and the solution boiled for a few minutes. A stream of carbonic acid gas was then sent through the dark-coloured liquid till all the caustic alkali was neutralized. The solution was then concentrated, and on its being set aside for some time, a quantity of scaly crystals was deposited. These crystals are the potash salt of a new acid which I shall call evernesic acid. They are very soluble in water and in hot spirits, but they may be washed with cold spirits without much loss. They are rendered quite colourless by digestion with animal charcoal. If the aqueous solution of the potash salt is decomposed by muriatic acid, a white flocculent precipitate is obtained. This precipitate readily dissolves in boiling water, and is deposited on the cooling of the liquid in long hair-like crystals of a silky lustre. These crystals are evernesic acid.

Evernesic acid may be still more advantageously prepared by employing baryta water instead of potash. When evernic acid is boiled for a short time in a slight excess of baryta water, much carbonate of baryta falls. This is to be removed and the solution saturated with muriatic acid, when the evernesic acid precipitates in silky needles which have a slightly yellowish tint. By being redissolved and treated with animal charcoal, they are rendered colourless. The mother-liquor from which the evernesic acid has been precipitated, when evaporated to dryness, yields a considerable quantity of orcin. Evernesic acid has neither taste nor smell. It is little soluble in cold, but very soluble in boiling water. It dissolves readily in hot spirits, and to some extent also in ether. Its aqueous and alcoholic solutions redden litmus paper. When heated in a test tube, it emits an agreeable smell and yields a white crystalline sublimate. Though orcin is always found in the mother-liquors from which the evernesic acid has been obtained, yet when evernesic acid itself is boiled a second time with either potash or baryta, no orcin is produced, showing that the orcin has been derived solely from the decomposition of *evernic* acid. Hypochlorite of lime merely gives a yellow colour with evernesic acid; and when it is dissolved in ammonia and exposed to the air, no red colour is produced. When evernesic acid was dried *in vacuo* and then at 212° F., it lost no water.

I. 0·191 grm. substance gave with chromate of lead 0·415 Co_2 and 0·0995 water.

II. 0·243 grm. substance gave 0·53 carbonic acid and 0·124 water.

	Calculated numbers.		I.	II.
18 C	1375·830	59·80	59·25	59·48
10 H	124·795	5·42	5·78	5·66
8 O	800·000	34·78	34·97	34·86
	2300·625	100·00	100·00	100·00

These analyses give $C_{18} H_9 O_7 + HO$ for the rational formula of hydrated evernesic acid.

Baryta Salt.

The baryta salt of evernesic acid is easily formed as follows. A quantity of evernic acid is boiled for a short time with a slight excess of baryta, and the solution neutralized by a stream of carbonic acid gas. The filtered liquid which contains the baryta salt and some orcin is to be evaporated to dryness on the water-bath. The orcin and the colouring matter which accompany the salt may be removed by treating the dry residue with either cold alcohol or ether, in both of which liquids the salt is nearly insoluble. If the salt is then digested in weak spirits, it readily dissolves, and is deposited on the cooling of the solution in large hard four-sided prisms arranged in a fan-like shape. If not quite colourless at first, the crystals may be easily rendered so by repeated crystallizations.

I. 0·228 grm. salt dried *two* days *in vacuo*, gave 0·083 BaO Co_2 = 0·0643 BaO = 28·20 per cent. BaO.

II. 0·355 grm. salt gave 0·5331 carbonic acid and 0·137 water.

	Calculated numbers.		I.
18 C	1375·8300	40·82	41·11
11 H	137·2745	4·07	4·28
BaO	956·8800	28·36	28·20
9 O	900·0000	26·75	26·41
	3369·9845	100·00	100·00

These numbers give $C_{18} H_9 O_7$+BaO+2 aq=*evern.* BaO+2 Aq.

I. 0·168 grm. salt dried *four* days *in vacuo*, gave 0·0635 BaO Co_2 =0·0492 BaO =29·28 per cent. BaO.

II. 0·1525 grm. salt dried *four* days *in vacuo*, gave 0·0577 BaO Co_2 =0·0447 BaO =29·31 per cent. BaO.

0·2091 grm. salt with chromate of lead gave 0·323 carbonic acid and 0·080 water.

	Calculated numbers.		Found. I.	II.
C 18	1375·8300	42·23	42·12	
H 10	124·7900	3·83	4·24	
BaO	956·8800	29·37	29·28	29·31
8 O	800·0000	24·57	24·36	
	3257·5000	100·00	100·00	

These numbers give $C_{18} H_9 O_7$+BaO+Aq for the rational formula of this salt of baryta = *evern.* BaO+Aq.

0·298 grm. same salt dried at 212°, gave 0·137 BaO So_3 =0·0899 BaO =30·16 per cent. BaO.

0·2611 grm. salt, also dried at 212° FAHR., gave 0·413 carbonic acid and 0·092 water.

	Calculated numbers.		Found.
18 C	1375·8300	43·74	43·13
9 H	112·3155	3·57	3·91
1 BaO	956·8800	30·42	30·16
7 O	100·0000	22·26	22·80
	3145·0255	100·00	100·00

The formula of this salt, which appears to be anhydrous, is $C_{18} H_9 O_7$+BaO=*evern.* +BaO.

It is evident from these results that evernesate of baryta exists in three states, viz. as an anhydrous salt, and with one and two atoms of water.

The Silver Salt.

The silver salt was formed by precipitating a neutral solution of evernesiate of ammonia with nitrate of silver; it is a white precipitate.

I. 0·247 grm. salt gave 0·092 silver =0·0988 AgO=40·00 per cent. oxide.

II. 0·141 grm. salt gave 0·053 silver =0·0569 AgO=40·35 per cent. oxide.

0·3835 grm. salt gave 0·522 carbonic acid and 0·1113 water.

	Calculated numbers.		Found.
18 C	1375·8300	37·80	37·12
9 H	112·3155	3·09	3·22
AgO	1451·6100	39·86	40·00
7 O	700·0000	19·23	19·66
	3639·7555	100·00	100·00

These numbers give $C_{18} H_9 O_7 + AgO$ as the formula of the silver salt, which, as might have been expected, is anhydrous, and agrees in this respect with the baryta salt dried at 212° Fahr.

Evernesic Ether.

A quantity of evernic acid was boiled for a short time in strong alcohol to which a few pieces of fused potash had been added, till the whole was dissolved. A current of carbonic acid gas was then sent through the dark-coloured solution till the caustic potash was saturated. On the cooling of the liquid a quantity of large brown-coloured prismatic crystals was deposited. These crystals were washed with cold water, in which they were nearly insoluble, and after being dried between folds of blotting-paper, and being repeatedly crystallized out of spirits, they formed beautiful white prisms about half an inch long. A further small quantity of these crystals was obtained by diluting the mother-liquor with water. The mother-liquor contains a considerable amount of orcin. A substance perfectly identical in its composition and properties with that just described, may also be obtained by boiling evernic acid in absolute alcohol for eight or ten hours. The alcoholic solution is then to be evaporated nearly to dryness by a gentle heat. The residue contains the ether mixed with a good deal of orcin, and some yellowish resinous matter. The orcin is removed by treating the mass with a little cold water, and the ether is freed from the resin which adheres to it very pertinaciously by digesting it with a little animal charcoal in dilute spirits. From the difficulty of separating the resinous matter from the ether, the first process with potash is by far the best.

The properties of the ether prepared by either of the above processes are as follows:—It has neither taste nor smell. It is very soluble in alcohol, whether hot or cold, and in ether. It is quite insoluble in cold water; boiling water dissolves little more than a trace of it. When heated to 133° Fahr. it melts, but crystallizes again when the temperature is slightly lowered. It is insoluble in ammonia, and gives no red colour with that alkali. Hypochlorite of lime has also no action upon it; its solutions give no precipitates with acetate or subacetate of lead. Cold and boiling muriatic acids produce no effect upon it. It is insoluble in carbonate of potash, but caustic potash dissolves it readily. The solution is colourless, and when it is neutralized by muriatic acid, the ether precipitates unchanged. Its alcoholic solution, when boiled with potash, yields no orcin and remains apparently unchanged. When however the vapour of the ether is passed over fused potash in a narrow glass tube with a capillary opening,

the ether is decomposed, and a gas is emitted which burns with the flame characteristic of alcohol. The potash when examined contained no orcin. There is every reason therefore to regard this substance as an ether.

I. 0·2482 grm. ether prepared with absolute alcohol and dried *in vacuo*, gave with chromate of lead 0·5740 carbonic acid and 0·1600 water.

II. 0·2774 grm. ether prepared in the same way, gave 0·640 carbonic acid and 0·171 water.

III. 0·373 grm. ether prepared with potash and alcohol, gave 0·859 carbonic acid and 0·228 water.

IV. 0·2617 grm. ether prepared with potash and alcohol, gave 0·604 carbonic acid and 0·1635 water.

	Calculated numbers.		I.	II.	III.	IV.
22 C	1681·570	63·30	63·07	62·92	62·80	62·94
14 H	174·713	6·58	7·15	6·88	6·79	6·93
8 O	800·000	30·12	29·78	30·20	30·41	30·13
	2656·283	100·00	100·00	100·00	100·00	100·00

$C_{18} H_9 O_7 + C_4 H_5 O$, the formula derived from these analyses, is exactly that which the evernesic ether ought theoretically to have, and which I am strongly inclined to think this substance most certainly is. It is no doubt somewhat singular that when an attempt was made to form the evernesic ether directly, by boiling evernesic acid in absolute alcohol saturated with muriatic acid gas, it totally failed. Still I am inclined to regard the substance above described as evernesic ether, as it certainly cannot be evernic ether, as might naturally have been expected, seeing that evernic acid was the acid employed in its formation; for its mother-liquors always contained orcin, thus showing that the evernic acid had been decomposed; and when the evernesic ether was fused with dry potash, it yielded no orcin, which evernic acid always does when similarly treated. It is clear therefore that the ether could not contain any evernic acid. The only probable explanation of this enigma appears to be that evernic acid does not form an ether, and that evernesic ether is only procurable when evernesic acid is generated in contact with alcohol.

On Orcin and its Preparation.

It is a remarkable circumstance that, so far as we know, orcin is always one of the products when any of the colouring principles of the lichens which yield red dyes with ammonia are subjected to particular operations. We have seen that this is the case with the principles of the different varieties of *Roccella tinctoria*, with those of the various kinds of *Lecanora*, and with that of the *Evernia Prunastri*. When the colouring principles of these lichens are destructively distilled, or are boiled with alkalies, or even with pure water or alcohol, orcin is always one, though by no means the only product. This circumstance is characteristic of this whole class of bodies,

and shows that though they differ considerably from each other in some respects, still a very intimate relation exists among them. Mr. SCHUNCK first observed that when lecanoric or erythric acids are boiled with an excess of any of the alkalies, orcin and a carbonate of the alkali are invariably produced. Mr. SCHUNCK was of opinion, and in this he has been followed by Messrs. ROCHLEDER and HELDT, that orcin and carbonic acids are the only products of this decomposition. We have already seen that this decomposition is by no means so simple as these gentlemen supposed; that, first of all, intermediate acids are always formed, and that in the case of the erythric and evernic acids, orcin is not the only ultimate product, but that pseudo-orcin and evernesic acid are also invariably obtained. Though orcin may be procured from (alpha) and (beta) orsellic acids, from erythric acid, and from lecanoric and evernic acids, they are not all of them equally suitable for this purpose. By far the best way, in fact the only way, of procuring colourless orcin, is to boil the (alpha) and (beta) orsellesic acids or erythrelesic acid in water from half an hour to an hour, when a great deal of carbonic acid is given off, and on the solution being concentrated and set aside to cool, abundance of colourless crystals of orcin are deposited. If a little animal charcoal is kept in the solution while it is being concentrated, it will be found useful in preventing any tendency to oxidation. I think it will also be found, though I have not had the opportunity of trying the experiment, that when lecanoric acid is neutralized with lime or baryta and boiled for a short time, it will be decomposed like orsellic and erythric acids, and yield an acid similar to the orsellesic and erythrelesic acids, which I have no doubt, by simply boiling in water, will also be converted into colourless orcin. By long-continued boiling with water, (alpha) and (beta) orsellic and erythric acids may no doubt be slowly converted into orcin without the intervention of an alkali. An immense amount of boiling is however required for this purpose. A quantity of orsellic acid which had been kept continuously boiling for three days, was only partially converted into orcin, and the product was far from colourless, owing to the effects of oxidation.

I. 0·332 grm. colourless orcin, prepared as above described, dried at the ordinary temperature, gave with chromate of lead 0·717 carbonic acid and 0·204 water.

		Calculated.	Mr. SCHUNCK's.	I.
16 C	1222·960	59·36	58·98	58·90
11 H	137·274	6·66	7·68	6·82
7 O	700·000	33·98	33·96	33·96
	2060·234	100·00	100·00	100·00

It will be seen from this that the faint red colour which orcin has when prepared by boiling with an excess of alkali, has no influence upon the analysis.

When it is wished to prepare orcin on a large scale without its being required to be perfectly colourless, the following process will be found very convenient. The clear solution obtained by macerating any of the varieties of the *Roccella tinctoria*, or

any of the different kinds of *Lecanora* in milk of lime, should be boiled in an open pan for some hours, and the liquid concentrated to about a fourth of its bulk. A stream of carbonic acid gas should then be sent through the liquid so long as carbonate of lime precipitates. The clear liquid should again be drawn off, and cautiously evaporated to dryness on the water-bath. The residue should then be boiled with three or four times its bulk of strong spirits, filtered and set aside to crystallize. In two or three days abundance of large dark-coloured crystals are deposited in the liquor. These should be separated and dried between folds of blotting-paper. The dried crystals should then be dissolved in three or four times their weight of anhydrous ether, in which they are exceedingly soluble, and the solution filtered. By evaporation *in vacuo* the orcin crystallizes out of the etherial solution in large six-sided prisms, which have only a light red colour, and which by a subsequent crystallization, also out of ether, may be rendered still fainter. A quantity of orcin prepared in this way was dried under the air-pump for upwards of a week. It is not easily dried, as it is a very hygroscopic substance. When subjected to analysis, it gave numbers which agreed exactly with those which Mr. SCHUNCK found for anhydrous orcin. Orcin repeatedly crystallized out of anhydrous ether appears therefore to be anhydrous. Orcin, however, is a substance which varies so much in the quantity of water it contains, according to the temperature at which it has been dried, that I defer saying more at present than that I am engaged in examining it more minutely.

When orcin is treated with a few drops of hypochlorite of lime, it assumes a dark purple red colour, which quickly changes to a deep yellow. It is quite different from the blood-red colour which orsellic or erythric acids yield when similarly treated, but it cannot be distinguished by the eye from the reaction which orsellesic and the other intermediate acids yield with hypochlorite of lime.

Brom-Orceid.

When bromine is poured into a concentrated aqueous solution of orcin an energetic action immediately ensues; much heat is evolved, and a brownish red crystalline mass falls to the bottom of the liquid. Bromine was added so long as this action continued, and the crystallized mass was separated from the supernatant liquor, which contained a great deal of hydrobromic acid, and was repeatedly washed with cold water. This bromine compound is but little soluble in either cold or hot water. In hot water it melts like a heavy oil, but crystallizes on the cooling of the liquid. It is very soluble in alcohol, both hot and cold, and also in ether. The brown colour of the crystals, when first precipitated, is owing to their being contaminated with a brown-coloured uncrystallizable resin. The quantity of this brownish resin is, comparatively speaking, small. It also contains bromine, and has a very pungent smell, which affects the eyes and nose very strongly, occasioning considerable pain. The crystalline bromine compound, which I shall call Brom-orceid, is readily purified by digesting it in dilute spirits, with the aid of a little animal charcoal, which absorbs

the brownish resinous matter. When pure, brom-orceid forms long white adhering needles. It has neither taste nor smell. The mother-liquors, from which it crystallizes, assume a pale reddish colour on standing, and contain some hydrobromic acid. The brom-orceid was dried *in vacuo* and subjected to analysis.

I. 0·355 grm. substance gave 0·5810 AgBr=0·2439 Br=68·70 per cent. bromine.
II. 0·407 grm. substance gave 0·665 AgBr=0·2792 Br=68·59 per cent. bromine.
I. 0·5442 grm. substance gave 0·471 carbonic acid and 0·076 water.
II. 0·451 grm. gave with chromate of lead 0·391 carbonic acid and 0·065 water.

	Calculated numbers.		Found numbers. I.	II.
66 C	5044·710	23·63	23·60	23·64
24 H	324·467	1·52	1·55	1·60
3 Br	14674·500	68·75	68·70	68·59
13 O	1300·000	6·10	6·15	6·27
	21343·677	100·00	100·00	100·00

The formula given above, $C_{66}H_{24}Br_3O_{13}$, is purely empirical. I regret that I have been unable to determine its atomic weight by the analysis of any of its compounds, and to establish a simple relation between it and orcin, if any such exist. Brom-orceid has a feeble acid reaction. It dissolves readily in alkaline solutions. These solutions soon grow dark-coloured, and when they are neutralized by muriatic acid, a yellowish resin precipitates.

Chlor-Orceid.

A similar compound is formed when chlorine is made to act upon orcin. In the course of several trials with dry orcin and with its aqueous and alkaline solutions, I obtained little more than traces of a crystalline chlorine compound. The crystals were always accompanied with a large quantity of a dark-coloured resin, which adhered to them so pertinaciously that I have not as yet been able to procure a sufficient quantity of the crystals to be able to subject them to analysis. Mr. Schunck endeavoured to prepare a similar compound, but, as he has given no analysis of it, I suspect that in this instance his success has been pretty similar with my own.

Usnic Acid.

This acid, which occurs in considerable quantity in several of the lichens, was discovered by Mr. Knop in 1843. It was also examined nearly at the same time by Messrs. Rochleder and Heldt. Knop found it in several species of Usnea, such as *Usnea florida*, *U. hirta* and *U. plicata*. Messrs. Rochleder and Heldt extracted it from the lichen *Rangiferinus*, *Usnea barbata* and *Ramalinea calicaris*. In addition to these sources, I may mention that I have found it in *Evernia Prunastri*, where it occurs along with evernic acid, and in *Ramalinea Fraxinea*. Knop's process for procuring usnic acid is by treating the lichens in a displacement apparatus with ether. This is

both a tedious and a costly method. Messrs. Rochleder and Heldt extracted it by macerating the lichens with a mixture of ammonia and spirits of wine. This latter method succeeds very well, but is also costly, especially in England, where alcohol is so dear. I have found that the method already so often described, viz. macerating the lichens in milk of lime and precipitating with muriatic acid, answers perfectly well, and is much to be preferred to either of the preceding methods. It is not advisable to employ either *Evernia Prunastri* or any of the species of Ramalinea for the preparation of usnic acid, as the acid obtained from these lichens is always accompanied with a good deal of resinous brownish colouring matter, which adheres to the acid so pertinaciously that it is very difficult to purify it completely. The lichens I prefer for the preparation of usnic acid are the *Cladonia Rangiferina*, but especially the *Usnea florida*. The lime solution of these lichens is deep yellow, and the precipitate thrown down either by muriatic or acetic acid has a bright yellow colour. By crystallizing this precipitate repeatedly out of alcohol, aided by a little animal charcoal, the usnic acid is obtained in large flat crystals of a pale-yellow colour. Usnic acid is not readily combustible.

0·2955 grm. acid dried at 212° Fahr. and burned with oxide of copper and a stream of oxygen gas, gave 0·688 carbonic acid gas and 0·134 water.

		Calculated.	Found numbers.
38 C	2854·56	63·90	63·62
17 H	212·16	4·75	5·03
14 O	1400·00	31·35	31·35
	4467·00	100·00	100·00

Potash Salt.

The potash salt was prepared in the way indicated by Mr. Knop, by boiling the acid with carbonate of potash. The salt crystallizes readily in large plates.

I. 0·407 grm. salt dried at 212° Fahr., gave 0·087 sulphate of potash =0·047 Ko =11·55 per cent.

II. 0·212 grm. salt gave 0·0453 $KoSo_3$=0·0244 Ko=11·50 per cent.

The calculated quantity of potash in the salt is 11·66 per cent.

Usnic acid is oxidized and converted into a dark brown uncrystallizable resin when it is boiled for a considerable time with an excess of either potash or baryta. The action of chlorine upon usnic acid produces a somewhat similar result.

Glasgow, January 25, 1848.